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# **The Formation of Colored Impurities in Triaminoguanidine Nitrate and Related Incompatibility Problems in Gun Propellants**

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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number)<br>A mechanism has been proposed for the formation of colored impurities in triaminoguanidine nitrate. It is suggested that the rate determining step for color formation is the production of the free base, triaminoguanidine, from triaminoguanidine nitrate. The multitude of colored impurities either arise from the metal ion induced oxidation or the aerial oxidation of triaminoguanidine or subsequent reactions of these oxidation products. The aerial |                                      |  |

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oxidation processes are enhanced in the presence of bases. The aerial oxidation process is also strongly catalyzed by metal ions. It is recommended that purification and storage of triaminoguanidine nitrate is best carried out in acidified water in non-metallic apparatus. The optimum conditions for the synthesis of triaminoguanidine nitrate, such that the production of colored impurities is minimized, would appear to involve an aqueous medium kept free of metal ions, minimal alkaline conditions and the absence of atmospheric oxygen. Propellants containing contaminated triaminoguanidine can undergo various color changes during manufacture which may cause porosity in the propellant, leading to enhanced and erratic burning rates. Strategies to minimize introduction of impurities which may cause incompatibility problems during the formulation of propellant are discussed.

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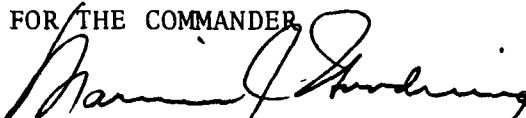
## PREFACE

This report documents work performed at the Air Force Armament Laboratory, Armament Division, Eglin Air Force Base, Florida, between August and September 1981 in support of Project 25600820. Dr. Clifford W. Fong of the Ballistics Branch, Direct Fire Weapons Division and Propulsion Division, Weapons System Research Laboratory, Defence Research Centre, Salisbury, South Australia, on assignment to DLDL, was the project engineer for this effort.

This report has been reviewed by the Public Affairs Office and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

FOR THE COMMANDER

  
MARVIN J. WOODRING, Colonel, USAF  
Chief, Direct Fire Weapons Division

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## SECTION I

### INTRODUCTION

Triaminoguanidine Nitrate (TAGN) is an essential ingredient in a new generation of gun propellants which have been shown to produce low flame temperatures and low gas molecular weights while providing increased muzzle velocity and impetus. However, although TAGN has been known for years to have favorable thermodynamic properties for use in cool burning gun propellants, concern has been voiced for many years over the appearance of colored impurities in the normally white TAGN. In particular, it is important to know if these colored impurities are detrimental to the stability of propellants containing TAGN.

Considerable effort has been expended at different laboratories over some 20 years in an attempt to track down the cause of the colored impurities (References 1 through 7). This study reviews these findings and postulates an overall mechanism for the formation of the colored impurities. Methodology to prevent the formation of the colored impurities rather than actual identification of the impurities, a formidable task, is the major concern of this study.

Efforts to formulate a rational mechanism for the TAGN decomposition process have been hampered by the voluminous evidence collected over many years which, at times, has seemed contradictory and ill conceived. Much effort has been aimed at identifying the many highly colored impurities which are usually only present in small quantities. However, since these efforts have been unsuccessful in identifying any of the colored impurities, it was considered that a better approach was to concentrate on formulating a kinetic scheme from those experimental observations where the presence of colored impurities were minimized or absent. Intuitive consideration of the possible compounds formed from TAGN which could be highly colored, as well as a knowledge of the chemistry of hydrazine type compounds (Reference 8) were essential in formulating a reaction scheme.



At present, little is known about the physical properties, burning rate properties, and stability of propellant containing colored or contaminated TAGN. Such propellants have often been observed to be tan or light brown colored, though little is known about their properties. It is important to know if contaminated TAGN will cause incompatibilities in propellant which may affect ballistic properties.

## SECTION II

### DISCUSSION OF THE MECHANISM OF COLOR FORMATION IN TRIAMINOGUANIDINE NITRATE

While the long term stability of crystalline TAGN under normal conditions has never been questioned, it has been repeatedly observed in various laboratories that purification and storage of TAGN in various solvents often lead to intensely colored solutions and colored crystals. Previous work (References 5 and 6) has indicated that the impurities which give rise to the intense colors are only present in very small quantities, of the order of one percent or less.

A consideration of possible compounds that can be formed from TAGN suggests that only compounds containing functional groups such as the azo ( $-N=N-$ ), imino ( $-C=N$ ), nitro ( $-NO_2$ ), or nitroso ( $-NO$ ) groups combined in highly conjugated systems would have extremely large extinction coefficients in the visible absorption spectral range. While the nitro or nitroso groups would undoubtedly arise from the nitrate moiety, the azo or imino groups can only arise from the oxidation of the hydrazine ( $-NH-NH_2$ ) moiety. The only common oxidant in the various studies previously reported (References 1 through 6) to give colored impurities is atmospheric oxygen. In view of the powerful reducing nature of hydrazino type compounds, this postulate seems entirely plausible.

Some speculative reaction processes which could give rise to intensely colored compounds are given in Figure 1. The major pathways to the formation of highly conjugated compounds containing the azo or imino type linkages involve oxidation by atmospheric oxygen. Secondary reactions such as those illustrated in Scheme 1, could involve nitric or nitrous acid reactions if these species were present. It is also apparent that, in view of the number of possible compounds containing more than one hydrazino group, an extremely complex mechanistic scheme involving competing parallel reactions could occur for any one compound containing the hydrazino moiety.

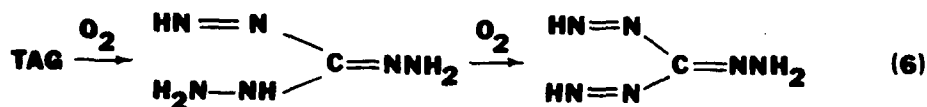
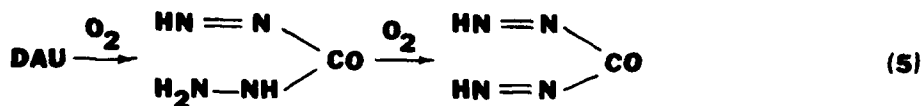
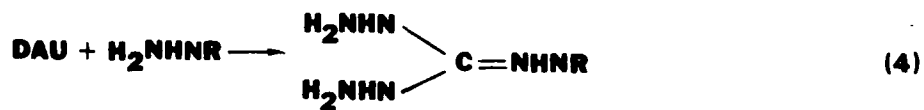
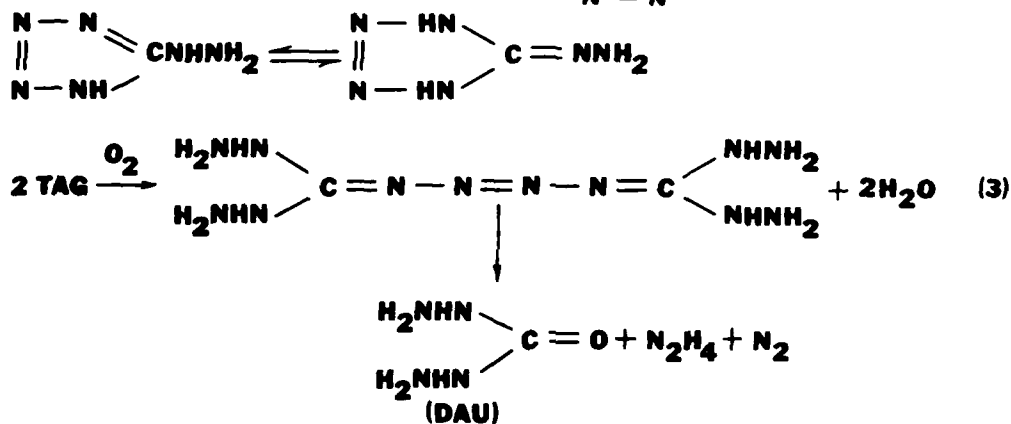
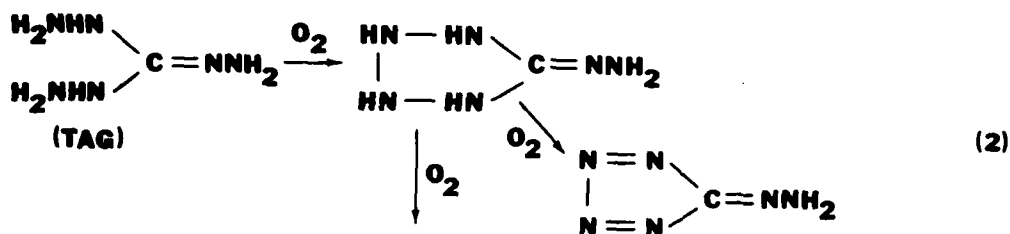
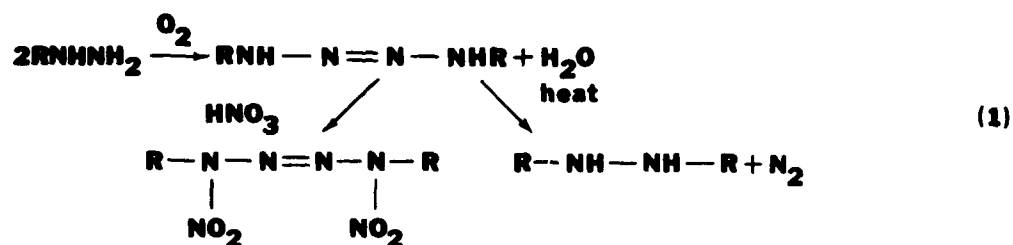


Figure 1. Possible Reactions of Triaminoguanidine Nitrate and Triaminoguanidine Which Can Give Rise to Intensely Colored Compounds

Intramolecular cyclization reactions such as those illustrated in Scheme 2 in Figure 1 could produce triazoles and other resonance stabilized heterocyclic ring compounds besides the tetrazoles illustrated in Scheme 2.

It has been reported earlier (Reference 3) that triaminoguanidine (TAG) is a white crystalline solid which is stable when stored in a vacuum or an inert atmosphere. However, in air the crystals turn pink and ultimately become deep purple. The colors result from small amounts of impurities only, as the infrared spectrum of the colored TAG is essentially that of pure TAG itself. Samples which become colored after exposure to air usually revert to a nearly colorless state again when resealed in a vacuum and allowed to stand. The colors rapidly reappear when the TAG is again exposed to air. In water, TAG is known to hydrolyze to diaminourea (DAU), a white compound, and hydrazine (References 3 and 5).

A probable mechanism for the aerial induced color changes of TAG is given as Scheme 3 in Figure 1. Oxidation by atmospheric oxygen gives the azo compound, which would be intensely colored, plus water as a by-product. Further reaction of the azo compound with the water would then give DAU and hydrazine, a process which does not require further oxygen to go to completion. The diazo compound could undergo further oxidation to tetrazole or triazole type compounds thereby inducing further color changes. Such a mechanism would explain the observed color changes of free TAG.

In view of the known aerial sensitivity of TAG, it seems highly likely that the observed color changes noted for TAGN occur via the free base, TAG. It is known that TAGN can be converted to its free base, TAG, by bases, strongly anionic ion-exchange resins (Amberlite IRA-400) or dimethylformamide (Reference 1). Conversely, pure (recrystallized) TAGN is known to be air stable in the solid state for long periods (References 1 through 7). Solutions of pure TAGN in distilled, deionized water do not show any color changes over several weeks, though a light yellow color can form on long term storage after several months (References 5, 6, and 7). A light yellow color

can also form when pure TAGN is heated in distilled deionized water for several hours at 90°C.

Thus the known aerial sensitivity of TAG and the relative inertness of TAGN strongly suggest the predominant pathway for color generation occurs via TAG. Hence if the formation of TAG from TAGN can be prevented, it should be possible to avoid color formation.

A further complicating factor in the formation of colored impurities in TAGN has been the observation in many laboratories (References 1 through 7) that various metals and metal ions can accelerate the rate of color generation. For example, a stainless steel thermometer dipped into a solution of pure TAGN in distilled, deionized water will produce an immediate pinkish color. Normally, such an aqueous solution of TAGN is stable in air for weeks (see above). Similarly, pure TAGN dissolves in normal tap water (which is known to contain a variety of metal ions) to form a pinkish solution (References 5 and 6).

A study by Chang et al (Reference 5), showed iron, nickel and cobalt salts added to aqueous solutions of TAGN immediately produced pink solutions, while chromium salts produced brown solutions. The concentration of the metal salts was roughly proportional to the intensity of the color produced, indicating that the rate of color formation is dependent upon the metal ion concentration.

A further major factor governing the rate of color generation is the pH of the TAGN solution. For example, while a saturated acidified aqueous solution ( $\text{HNO}_3:\text{H}_2\text{O}$  was 1:15) of TAGN showed no color generation over 12 months, a saturated basic solution ( $\text{NH}_4\text{OH}:\text{H}_2\text{O}$  was 1:15) of the same TAGN went pink in 2 weeks and eventually formed a homogeneous solution on longer term storage (Reference 6). As TAGN is known to be only slightly soluble in pure water (5.5 percent at 30°C and 7.5 percent at 40°C), it is obvious TAGN reacts completely to form other colored species in basic solutions. Similar tests have shown that the rate of color formation is strongly dependent upon the pH of the solution (References 5 and 7). Generally, mildly acidified aqueous solutions of pure TAGN in

deionized water are stable for long periods. However, color formation is rapid at pH>7. In the presence of metals or metal ions, color formation can occur at pH<7.

That color generation in aqueous solutions of TAGN is basically an oxidation reaction can be shown by the following experiments. Under a nitrogen atmosphere, alkaline solutions of TAGN do not form colored impurities. However, the instant air is admitted into the reaction vessel, the solution rapidly turns reddish purple. Hence, as predicted earlier from a consideration of possible reactions which could lead to highly colored compounds, aerial oxidation is the prime cause of color formation in solutions of TAGN. The aerial oxidation process is pH dependent and catalyzed by metals or metal ions. A mechanistic scheme which explains the above observations is given in Figure 2.

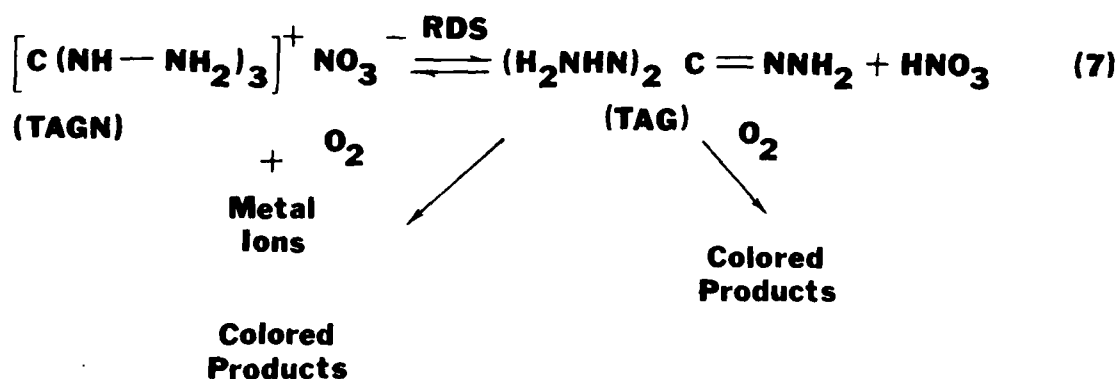


Figure 2. A Mechanistic Scheme for the Formation of Colored Impurities from Triaminoguanidine Nitrate

The rate determining step (RDS) for color formation is the reversible equilibrium between TAGN and TAG and nitric acid. The aerial oxidation reactions are non-reversible, and produce the various colored impurities via schemes such as those outlined in Figure 1. While the above reaction scheme was deduced from observations of color formation in solution, the scheme also explains various observations of color changes in TAGN crystals when heated in drying ovens. These aspects will be covered later in the text.

As indicated, the key to color formation is the dissociation of TAGN into TAG and nitric acid. Essentially, it should be possible to prevent the formation of colored impurities by driving the equilibrium to the left by addition of nitric acid to solutions (aqueous or organic) of TAGN. Thus the observation that an acidified aqueous solution of TAGN ( $\text{HNO}_3:\text{H}_2\text{O}$  was 1:15) was stable in the atmosphere for 12 months reflects the situation where the concentration of oxidisable TAG is kept extremely low. However, a basic aqueous solution ( $\text{NH}_4\text{OH}:\text{H}_2\text{O}$  was 1:15) led to the complete breakdown of TAGN over several months, since the base,  $\text{NH}_4\text{OH}$  removed the free nitric acid (to  $\text{NH}_4\text{NO}_3$  presumably) and displaced the equilibrium to the right. Hence, the concentration of the oxidisable species, TAG, was kept high, allowing aerial oxidation to the various colored species.

The very slow color formation of solutions of pure TAGN in distilled deionized water over many months results from the oxidation of the very small amount of TAG present under these equilibrium conditions. The likelihood that TAGN itself could undergo aerial oxidation can be ruled out by analogy\* with the fact that the hydrazinium  $\text{NH}_2\text{-NH}_3^+$  ion is known to be resistant to aerial oxidation (Reference 8). However, it is possible that metal oxides, such as  $\text{Fe}_2\text{O}_3$  and other iron oxides and hydroxides present in rust, could neutralize the free nitric acid formed in the RDS, and later act as catalysts in the aerial oxidation of the TAG.

The aerial oxidation of TAG can apparently occur via independent pathways. The postulate that two oxidation pathways exists is based upon the observation that color formation can still occur in pure distilled, deionized water solutions of TAGN. However, this reaction is far slower than the rate of color formation which occurs in the

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\* The chemistry of TAGN and TAG would be expected to be similar to the chemistry of hydrazine, the parent compound. TAGN and TAG may be considered as monosubstituted hydrazines ( $\text{RNHNH}_2$ , where  $\text{R}=(\text{H}_2\text{NHN})_2\text{C}^+$  - for TAGN, and  $\text{R}=(\text{H}_2\text{NHN})\text{C}(=\text{NNH}_2)$  - for TAG). While the R group for TAG would behave electronically as a substituted alkyl group, the R group for TAGN is an integral part of a cationic conjugated network (Reference 9).

presence of metal ions. However, the most efficient pathway is the metal (or metal ion) catalyzed aerial oxidation. The greatest rate of color formation will then be in basic conditions, in the presence of metal ions in the open atmosphere. This situation is entirely analogous to the known aerial oxidation (Reference 8) of hydrazine. The oxidation of hydrazine does not occur in aqueous acid solutions (where it exists as the hydrazinium ion), but occurs most readily in basic conditions and is strongly catalyzed by many transition metal ions. For example, in the autoxidation of hydrazine by ferricyanide, the reaction is pseudo third order, being dependent upon the concentration of the hydrazinium ion, hydroxyl ion and ferricyanide ion.

It would appear as if the autoxidation of TAG, like that of hydrazine, can be similarly pseudo third order. It was noted earlier in the text that the rate of color formation was roughly dependent upon the concentration of metal ions. The reaction scheme depicted in Figure 2 requires a concentration dependence upon base (to remove nitric acid and move the equilibrium to the right) and substrate if the rate of color formation is to be maximized.

The known oxidation potentials for hydrazine in basic, neutral and acidic media should be good indicators of the ease of oxidation of TAGN and TAG in similar media. The  $E^0$  values for hydrazine are: (a) in base (1M NaOH, 3M NaCl): 0.05 volts (Reference 10); (b) in water: 0.15 volts (Reference 8); (c) in acid solution (as the  $N_2H_5^+$  ion): 1.27 volts (Reference 8). Obviously, the  $N_2H_5^+$  ion is orders of magnitude more resistant to oxidation than the free hydrazine molecule in solution. Hydrazine is most easily oxidized in basic solution.

The first step in the  $Ce^{4+} + Ce^{3+}$  oxidation of hydrazine involves the formation of the  $N_2H_4^{+\cdot}$  cation radical species (Reference 11), which is followed by rapid deprotonation etc. In view of the known stability of hydrazine in acid solution to oxidation (presumably because the cation radical species is not easily formed from the  $N_2H_5^+$  ion), it is predicted that TAGN, a cationic species, would

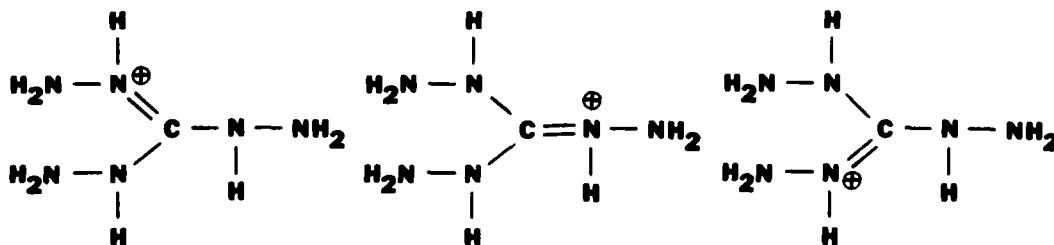


also be similarly resistant to oxidation.\* However, TAG, a neutral molecule with an imino nitrogen atom, would be expected to form a cation radical with ease (References 12 and 13). The immediate reddish color formation of TAG when in contact with air may indeed be due to the formation of the intermediate cation radical species during the oxidation process.

The powerful catalytic effect of metal ions in producing colored contaminants in TAGN solutions is illustrated by the observation that a saturated solution of twice recrystallized TAGN in dilute aqueous acid ( $\text{pH} \approx 1$ ) slowly goes yellow within 3 to 4 days in the presence of added rust, and copper ions. As the proportion of free TAG in dilute aqueous acid should be extremely low, the rate of aerial oxidation in the presence of transition metal ions must be extremely rapid. As previously noted, pure TAGN in aqueous acid solution ( $\text{pH} \approx 1$ ) does not show any color formation over many months. As a large number of the transition metal ions in high oxidation states have high oxidation potentials (greater than that of oxygen,  $E^0 = 0.68$  volt), it will be mainly the transition metal ions which will catalyze the aerial oxidation process rather than the main group metal ions.

A more detailed version of the mechanistic scheme in Figure 2 can be written to accommodate the likely oxidation reactions (Figure 3).

\* The structure of TAGN can be represented by the canonical contributors:



As the C-N bonds are of equal length (Reference 9), the N atoms possess equal partial positive charge, and hence are quasi iso-electronic to the N atoms in the  $(\text{NH}_2-\text{NH}_3)^+$  cation.

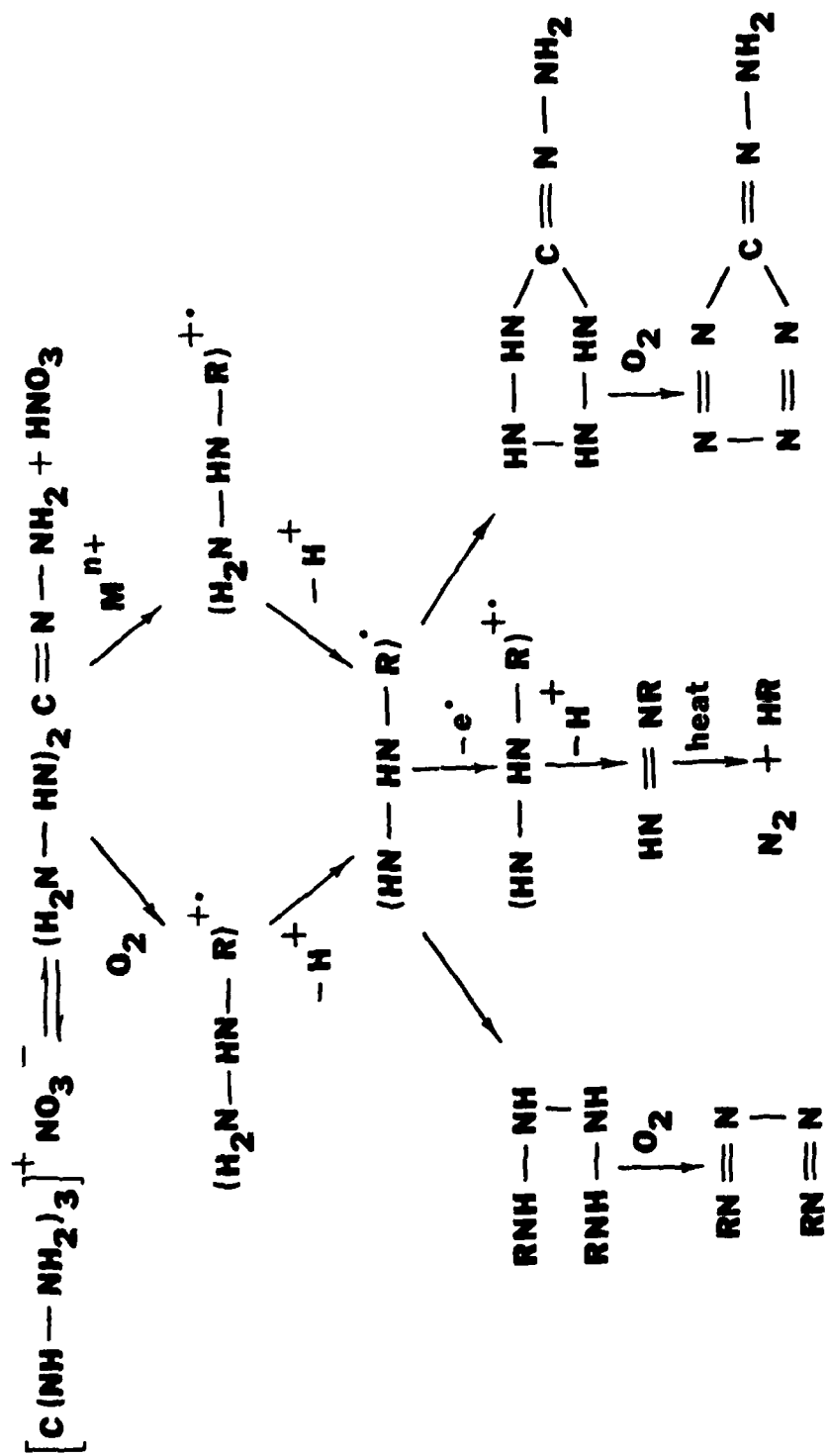


Figure 3. A Mechanistic Scheme for the Oxidation of Triaminoguanidine by Atmospheric Oxygen or Metal Ions

The formation of the cation radical species from TAG could proceed via two independent pathways: aerial oxygen or metal ion induced electron transfer, with the latter process favored for metal ions which have greater redox potentials than that for oxygen ( $E^0=0.68$  volt). The deprotonation of the cation radical could be achieved by any base: other TAG molecules, other hydrazino groups on the same molecule, metal oxides and hydroxides, basic impurities in the solvent and possibly even reaction with alcohol, water, ethyl acetate molecules, etc. It is likely that where metal ions are present as insoluble metal oxides or hydroxides (e.g. rust), the oxidation process and deprotonation reaction could occur on the surface of the metal oxide. Such a postulate would explain the observed color formation of TAGN samples in highly acidic media in the presence of added rust.

Some of the oxidation products could be expected to undergo further hydrolysis (to DAU for example) or thermolysis, involving the thermodynamically favorable formation of free nitrogen gas. Thermolysis of oxidation products in contaminated TAGN could be a major incompatibility process in TAGN containing gas propellants.

The formation of color in TAGN can only occur in solution. It has been often observed that pure dry samples of TAGN are stable in the open atmosphere for years. However, "impure" samples of TAGN can turn colored when damp with organic solvents or even in a humid atmosphere when heated in drying ovens. Samples of TAGN stored for long periods in various organic solvents such as isopropyl alcohol, ethyl acetate, ethyl alcohol, freon, etc. are known to form colored impurities at various rates (Reference 6). However, generally only the solutions are colored, or the outer surface of the crystals are colored, hence allowing the colored impurities to be washed away with fresh solvent. All observations of color formation in saturated solutions of TAGN are consistent with aerial oxidation occurring in solution only, and not in the solid state.

However, isopropanol moist crystalline samples of TAGN have been known to turn pink then blue when stored in a  $49^{\circ}\text{C}$  oven (References 7

and 14). Acidic fumes were also given off (pH of a saturated solution in water was 2.8) during the heating process. It is known though, that this particular batch of TAGN had been in intimate contact with a metal stirrer and consequently had been contaminated by metal ions. Apparently, the presence of metal ions and the high temperatures accelerated the formation of the colored impurities even though the amount of solvent was minimal. The free acid formed is then consistent with displacement of the TAGN to TAG equilibrium (reaction 7) to the left. Upon further drying of the colored TAGN, and breaking up and spreading out the lumps of agglomerated crystals (which contain trapped solvent), the crystals eventually turned white again. Thus, in the absence of solvent, the complex color forming reactions of the free TAG cease, and presumably result in the formation of colorless DAU. However, if this TAGN is again stored as a saturated solution in pure deionized water (pH=6), a yellow solution results within 1 day at room temperature (various other control batches of TAGN under the same conditions remained colorless for weeks).

The many observations that the "purity" of the crystalline TAGN can strongly influence the rate of formation of colored impurities in solution (References 5 and 6) is explicable in terms of the varying trace amounts of metal ions present in the crystalline material (though metal ions present in the storage solvents will also catalyze the aerial oxidation process). Hartman et al have shown that twice recrystallized TAGN, when stored in isopropanol, still produced colored solutions at a greater rate than the same batch of TAGN stored in ethanol, water or freon. However, a control sample of TAGN also produced colored solutions in isopropanol at a greater rate than the sample of TAGN in ethanol, water or freon, but at a slower rate than the sample of TAGN in isopropanol (see Figure 7 in Reference 6). The difference between the sample and control batches of TAGN can only to be attributed to some impurity in the TAGN batches. The most likely contaminant would be trace metal ions (possibly co-crystallized as metal chelate complexes) in view of the high rate of color formation. As the metal ion concentration in the various solvents is unknown, it is difficult to decide whether the different

rates in the various solvents are due to impurities in the solvents or to the intrinsic nature of the solvents themselves (excluding freon, when solubility effects are operational).

Another factor which will influence the "purity" of crystalline TAGN is the amount of base occluded in the crystals. It is well established that high Taliani gas generation rates in crystalline TAGN can be traced to occluded solvent (References 5 and 6). It is also observed that repeated recrystallizations will lower the pH of a saturated solution of TAGN, often from a pH value greater than 7 to a value less than 7 (Reference 6), usually averaging a value of ca. 5.5. Thus, the entrained liquid in the TAGN crystals is often basic (the pH of the synthesis medium is always basic). Hence a combination of trace metal ions and occluded base in the TAGN crystals can influence the rate of color formation.

From the above discussion, recrystallization of TAGN is best carried out in acidified, deionized water (pH:5) in an all glass apparatus. The possibility of entraining basic liquids in the crystals will then be eliminated.

The preparation of TAGN from cyanamide (References 1, 2, and 4) or guanidine nitrate (References 4 and 6) requires an excess of hydrazine to produce high yields. The reaction medium is consequently always basic, and would be expected to produce colored oxidation products even if metal ions were rigorously excluded by using all glass apparatus and metal ion free reagents. The obvious method to prevent color formation in the reaction medium is to use an inert atmosphere (e.g. nitrogen) during the preparation, then acidify the filtrate immediately the reaction is completed. The possibility of aerial oxidation will be greatly reduced in acidic medium allowing isolation and purification in the open atmosphere.

It is also apparent that industrial grade isopropanol stored in metal containers contains significant quantities of metal ions, especially  $\text{Fe}^{n+}$  (Reference 5). Other industrial grade solvents such as ethanol, ethyl acetate, etc., will almost certainly contain trace amounts of metal ions. The least expensive commonly available solvent

which could be obtained metal ion free is deionized water. The use of water as the reaction medium would also simplify purification and long term storage.

The best solvent for long term storage of TAGN would appear to be acidified water (pH=5) despite the fact TAGN is soluble in water (ca. 5.5 percent at 30°C). However, the TAGN would only need to be damp with acidified water. Hexane or other hydrocarbon solvents would also be good storage solvents since they are chemically inert and TAGN is insoluble in these solvents. While TAGN is similarly insoluble in Freon 113, this solvent is not as chemically inert as the hydrocarbon solvents.

### SECTION III

#### DISCUSSION ON THE EFFECT OF COLORED IMPURITIES IN TRIAMINOGUANIDINE NITRATE AND THE STABILITY OF GUN PROPELLANTS CONTAINING TRIAMINOGUANIDINE NITRATE

Hartman et al (Reference 6) have recently concluded from Differential Scanning Calorimetry (DSC) and stabilizer depletion studies/accelerated aging studies of gun propellant made from colored TAGN that colored TAGN has no deleterious effects. However, they did suggest that propellant made from colored TAGN did tend to more acid values with aging time than did propellant made from white TAGN. Unfortunately, DSC is not a sensitive indicator of propellant stability, especially if only minor contaminants are involved.

Experience with TAGN gun propellant at Eglin AFB is not so optimistic, however. Burning rate propellant strands made from various batches of TAGN (from several sources, Rocketdyne and Allegany Ballistics Laboratory, ABL) have shown up some major incompatibility problems, all traceable to the purity of the TAGN in the propellant (References 7, 14 and 15).

The worst example of incompatibility in a standard formulated propellant (containing nitrocellulose, 25.0 percent, TAGN, 70 percent, dibutyl phthalate, 4.8 percent, resorcinol, 0.2 percent) was a propellant which was light green in the mixer, blue after extrusion and dark blue with wet spots on the surface after drying in an oven for a day at 43°C. The wet spots were presumably nitric acid, as the oven had an acrid odor. Upon further drying at 60°C the strands turned brown, but still showed wet spots on the surface. The unground TAGN (batch 2.7.1) used in the propellant had been stored for a long period in isopropanol and as received consisted of white crystals in a clear solution of isopropanol. The TAGN turned brown when dried from the isopropanol in an oven at 60°C. The high pressure linear burning rate data was erratic and non-reproducible.

Thorough washing of batch 2.7.1 TAGN with isopropanol or isopropanol/hexane before incorporating in an identical formulation produced white mixes of propellant which only turned light brown when dried at 60°C. However, the strand burning rate data was still

erratic and non-reproducible. Various batches of the same formulation of propellant made from batch 2.7.1 TAGN ground in hexane and freon (to ca. 5 $\mu$  particle size) also produced tan colored propellant which showed erratic linear burning rates. Recrystallization of batch 2.7.1 TAGN twice from deionized water in all glass apparatus, followed by grinding in isopropanol also produced tan colored propellant with purplish black spots and purplish black voids in the propellant. As the propellant was white prior to drying at 60°C, the tan and purplish black colors can only be due to heat assisted aerial oxidation of the TAGN, and the purplish black holes due to local concentrations of processing solvent in TAGN crystal agglomerates where aerial oxidation produced relatively high concentrations of either free HNO<sub>3</sub> (or gases derived from reactions of HNO<sub>3</sub>) or N<sub>2</sub> gas from thermolysis of oxidation products. Similar tan colored propellant with purplish black spots and voids has also been made from other TAGN batches derived from different sources. It should also be noted that tan colored propellant has also been made elsewhere (Reference 16). All TAGN containing propellant made at Eglin AFB has been tan or light brown colored and the linear burning rate data has varied from acceptable to highly erratic and non-reproducible (the majority of propellants).

The problems associated with gun propellant manufactured at Eglin may be due to a variety of causes:

- (a) impure TAGN containing entrained base or metal ions;
- (b) pure TAGN stored for long periods in isopropanol during storage and transported to Eglin; isopropanol can contain metal ion impurities;
- (c) recrystallization from water can improve the final propellant as adjudged from less scatter in the strand burning rate data; however, this is not always so;
- (d) grinding the TAGN in isopropanol in a SWECO mill which has a metal lid; both solvent and the SWECO could lead to metal ion contamination; ethyl acetate, freon, hexane have also been used as grinding diluents, however, the propellant was still tan colored;
- (e) drying the ground TAGN at 60°C in a forced air oven (in a high humidity atmosphere) can lead to lumps and agglomerates of crystals; heating the TAGN in metal contaminated solvent may speed up aerial oxidation; a vacuum oven has been used to dry the TAGN, and the final propellant was cream colored;



- (f) the propellant is often white when extruded but rapidly turns tan colored when dried at 60°C in a forced air oven; heat facilitated aerial oxidation in the damp propellant can turn the propellant tan colored (or other colors) or produce purplish black spots or purplish black voids; the procedure used to dry burning rate strands at Eglin (and elsewhere) may exacerbate the heat facilitated aerial oxidation of TAGN in the propellant, since a slow controlled evaporation of solvent is required to produce straight uniform strands; it is expected that the drying of propellant grains will be far more rapid (due to increased surface area), hence reducing the possibility of heat assisted oxidation of TAGN in the residual processing solvent; however, predominantly white grains with dark brown spots and tan colored grains have been observed for TAGN containing gun propellants (References 14 and 15).

It is unknown which of the above six factors are the cause of the incompatibility. Dry grinding the TAGN in a Jet-o-Mizer would eliminate factors (d) and (e) as sources of incompatibility. Storage and transport in isopropanol should cease, and be substituted by storage in acidified water or hexane to eliminate factor (b). Drying of damp propellant in an inert atmosphere would minimize aerial oxidation (factor f). Evidence from several sources suggests recrystallization of TAGN from deionized water does not completely eliminate impurities (References 7, 14, 15 and 16). However, lack of control elsewhere in the formulation procedure may complicate this finding; conversely it may be inherently difficult to remove metal ions completely from contaminated TAGN. The easiest route to avoid this problem would be to prevent introduction of metal ions by rigorous quality control during synthesis and the formulation cycle.

Strong evidence (Reference 17) that the purity of the TAGN as well as the grinding conditions can affect the stability of the resultant propellant comes from data collected from modified Taliani tests (90°C for 23 hours) for a series of propellants containing TAGN, NC, DBP and NDPA formulated in ethyl acetate (Table 1). The various batches of TAGN were first noted to be either basic, neutral or acidic in solution then formulated into propellant either as ground or unground TAGN. Wet grinding of the TAGN in ethyl acetate was conducted either in a stainless steel SWECO mill or a porcelain laboratory ball mill.

TABLE 1. MODIFIED TALIANI RESULTS - TAGN WITH SINGLE BASE\*

| Sample     | Treatment                   | MP<br>(°C) | Pressure<br>(mm at 23 hr) |
|------------|-----------------------------|------------|---------------------------|
| Rocketdyne | Unground, Neutral           | 220        | 66                        |
| Rocketdyne | Ground, 5 $\mu$ , Neutral   | 218        | 51                        |
| ABL        | Unground, Basic             | 218        | 53                        |
| ABL        | Unground, Acid              | 220        | 30                        |
| ABL        | Unground, Neutral           | 219-220    | 21                        |
| ABL        | SWECO, 2 $\mu$ , Neutral    | 219        | 109                       |
| ABL        | Lab Mill, 3 $\mu$ , Neutral | 220        | 78                        |
| ABL        | Basic, SWECO, 2 $\mu$       | 216        | 264                       |

\*Tested with NC, DBP and NDPA blend in ethyl acetate.  
From Reference 17.

Inspection of Table 1 reveals:

- that grinding neutral TAGN in a SWECO mill results in a propellant whose Taliani value has significantly increased from 21 mm (for unground neutral TAGN containing propellant) to 109 mm;
- however, that ground neutral TAGN (from the laboratory ball mill) results in a propellant whose Taliani value has increased from 21 mm (for unground neutral TAGN containing propellant) to 78 mm; this result indicates a significant destabilizing effect when neutral TAGN is ground in a stainless steel mill compared to when the TAGN is ground in a porcelain mill;
- a dramatic increase in the Taliani value for propellant made from basic TAGN ground in a SWECO mill (from a value of 33 mm for the unground basic TAGN to 264 mm when the TAGN is ground in a stainless steel mill); this large increase in the instability of propellant containing basic TAGN ground in metal containing apparatus is further evidence of the incompatibility of TAGN, metal ions and base.

It should be noted that unground TAGN has been shown to contain occluded solvent water (Reference 6) so normally the Taliani values decrease when the TAGN is ground.

Further evidence that wet grinding TAGN in a stainless steel mill gives rise to major contamination of the TAG is also apparent when comparing Taliani values (modified Taliani with NG at 90°C)

before and after lining the SWECO mill with a polyurethane liner (Reference 17). Before lining the mill, the values were unacceptable at greater than 200 mm, but after lining the mill, the values dropped to ca. 60 mm. The polyurethane liner obviously decreases the contact of the TAGN with metal.

The incompatibility of basic compounds with TAGN has important ramifications in the choice of stabilizers for propellant containing TAGN. Some previously unexplained results (Reference 16) from stabilizer compatibility trials with a propellant formulation containing 50.0 percent TAGN, 17.7 percent HMX, 5.0 percent IDP, 17.9 percent NC and 0.4 percent stabilizer (Table 2) strongly support this notion. Table 2 indicates that 2-nitrodiphenylamine (NDPA) and ethyl centralite (EC) give very high Taliani slopes in this propellant (1.84 and 2.25 mm Hg/min, respectively), compared to the Taliani slope for a propellant with no stabilizer (0.91 mm Hg/min). It is obvious that the strongly basic NDPA and EC are actually destabilizing the propellant. However, resorcinol does stabilize the propellant (the slope is 0.37 mm Hg/min) significantly compared to the value of 0.91 mm Hg/min for propellant with no stabilizer present. As NDPA, EC and resorcinol are widely used stabilizers in other propellants containing nitroesters, the enormous difference between the NDPA and EC stabilizers and resorcinol can only be due to the fact the former two stabilizers are strong bases while resorcinol is an acidic compound. An interesting peripheral result is the observation that the combined stabilizer systems EC/resorcinol and NDPA/resorcinol are about as efficient as resorcinol alone and far more efficient than EC or NDPA alone. This result can only be explained if resorcinol forms ionic complexes with both EC and NDPA by protonation, and that the resultant complexes are equally efficient stabilizers as is resorcinol.

The Taliani results in Tables 1 and 2 are evidence for a decomposition pathway of TAGN which may proceed via metal ion promoted electron loss (oxidation) of TAG (formed from deprotonation of TAGN by base) in the absence of air (since Taliani tests are done in a nitrogen atmosphere). Deprotonation of the cation radical (see Figure 3) can then occur via any basic compound available, for

example, basic stabilizers, other TAG molecules, other hydrazino groups on the same molecule, metal oxides or hydroxides, etc. It is not suggested that anaerobic metal ion induced oxidation of TAG is a major pathway under ambient conditions, but only that such a process can occur at high temperatures. As indicated in Section II, the major pathway for the formation of colored impurities in TAGN under ambient conditions involves metal ion catalyzed aerial oxidation of TAG in solution.

TABLE 2. TALIANI RESULTS AT 110°C FOR VARIOUS STABILIZERS ADDED TO A PROPELLANT CONTAINING 59.0 PERCENT TAGN, 17.7 PERCENT HMX, 5.0 PERCENT IDP, 17.9 PERCENT NC (12.6 PERCENT N) AND 0.4 PERCENT STABILIZER

| Stabilizer                          | Total Pressure Rise<br>in 90 Minutes | Slope at 90 Minutes<br>(mm Hg/min) |
|-------------------------------------|--------------------------------------|------------------------------------|
| None                                | 82                                   | 0.91                               |
| 0.4% 2-Nitrodiphenylamine<br>(NDPA) | 165                                  | 1.84                               |
| 0.4% Ethyl Centralite (EC)          | 203                                  | 2.25                               |
| 0.4% Resorcinol (RES)               | 38                                   | 0.37                               |
| 0.2% EC/0.2% RES                    | 34                                   | 0.34                               |
| 0.2% NDPA/0.2% RES                  | 51                                   | 0.48                               |
| From Reference 16.                  |                                      |                                    |

Propellant manufactured from "impure" TAGN may contain varying degrees of porosity, from microporosity which would be manifested in a "fast" burning propellant or colored macroscopic voids as observed in some burning rate strands manufactured at Eglin. Propellant grains prepared to a standard formulation is generally fast when manufactured from "impure" TAGN, indicating the presence of microporosity (Reference 16).

Figure 4 shows the strand burning data of four propellants (GP 172, GP 200, GP 218 and GP 219) made to the same standard formulation (as described above) from the same batch of TAGN (lot 74) (Reference 14). The TAGN, as received, consisted of white crystals in a brown solution of isopropanol. Propellant GP 172 was manufactured from ground TAGN which had been washed with isopropanol.

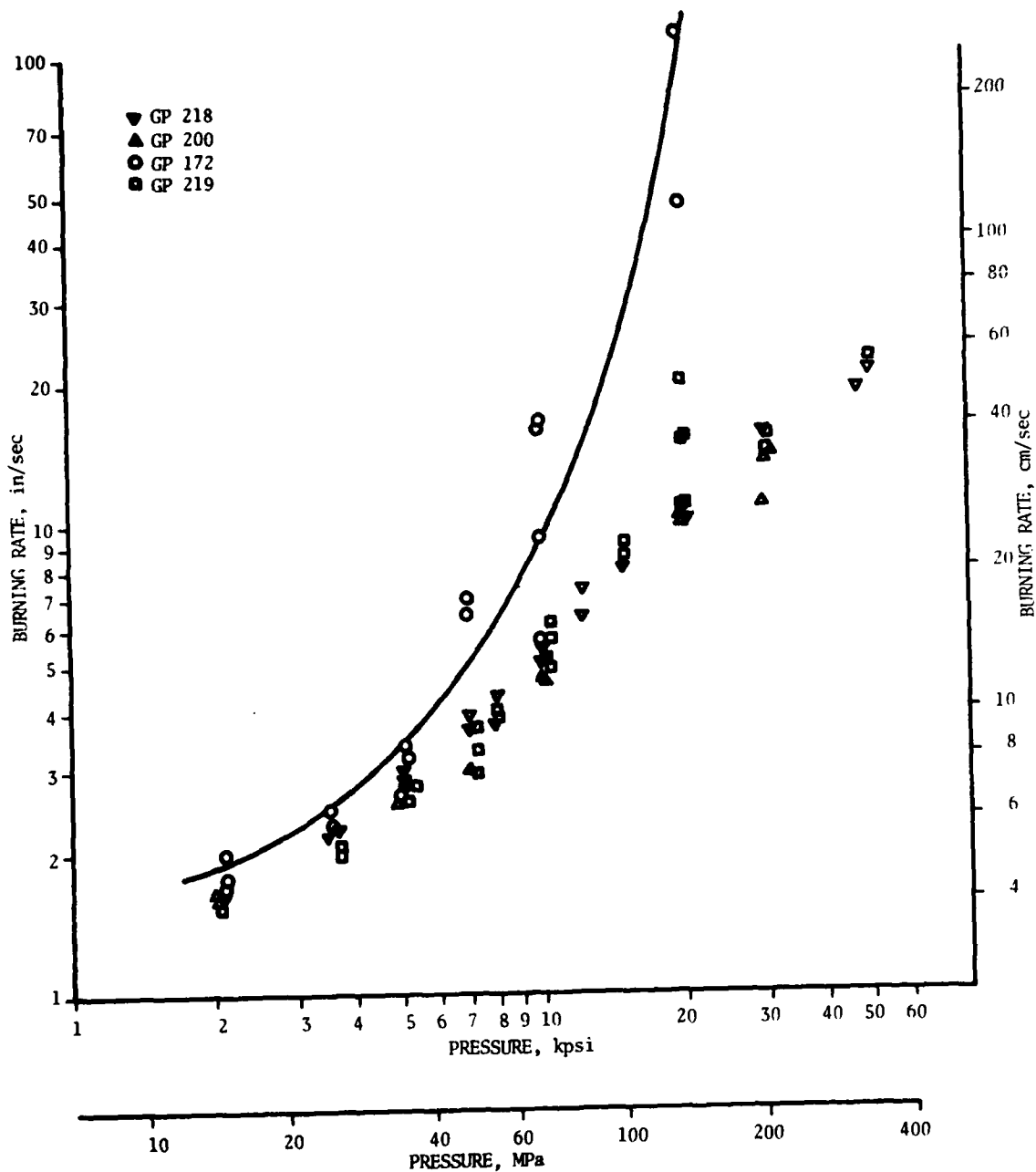


Figure 4. Burning Rates of Four Standard Formulated Propellants Containing TAGN (70 Percent) from the Same Batch; Propellant GP 172 Contained Unrecrystallized TAGN, Whereas Propellants GP 200, GP 218 and GP 219 Contained Recrystallized TAGN

Propellant GP 200, 218 and 219 were made from recrystallized TAGN which had been ground in isopropanol and thoroughly washed with isopropanol or isopropanol/hexane. All four propellants were a tan color. It is immediately obvious that propellants GP 200, 218 and 219 are quite consistent and reproducible (with the exception of a small amount of scatter at 20,000 psi for GP 219). The burning rates at some 9, 12 and 13 pressures (duplicate measurements, sometimes triplicate measurements) were measured for propellants GP 200, 218 and 219 respectively. Hence a high degree of confidence can be placed on the best fit burning rate curve for these propellants. However, propellant GP 172 shows enhanced burning rates compared to those of propellants GP 200, 218 and 219, and displays erratic and non-reproducible burning behavior. It can be concluded that recrystallization of the TAGN has removed some impurity which causes microporosity in the propellant, leading to an enhanced and erratic burning rate for propellant GP 172. As all four propellants showed signs of color incompatibility in the TAGN, it is likely that the unrecrystallized TAGN contained a greater concentration of the color-forming impurity.

Figure 5 shows the burning rates of three propellants made to the same standard formulation as those shown in Figure 4. The TAGN originated from different manufacturers and had been stored isopropanol wet for long periods at Eglin AFB. Batch 2.7.1 of TAGN was carefully recrystallized twice from deionized water before formulation. Batches 2.7.5 and ABL of TAGN were thoroughly washed with isopropanol to remove the yellow storage solvent before grinding. All burning rate strands were dark tan colored with purplish black spots and purplish black voids in the propellant. It can be clearly seen from Figure 5 that the triplicate burning rates for the three supposedly identical propellants are highly scattered and non-consistent. If the burning rates for propellants GP 200, GP 218 and GP 219 in Figure 4 are compared with the burning rates in Figure 5, it can be seen that the burning rates of the three propellants made from batches 2.7.1, 2.7.5 and ABL TAGN all exhibited marked degrees of enhanced burning rate due to porosity (which can be visually observed under the optical microscope) in the propellant (Reference 7). It is

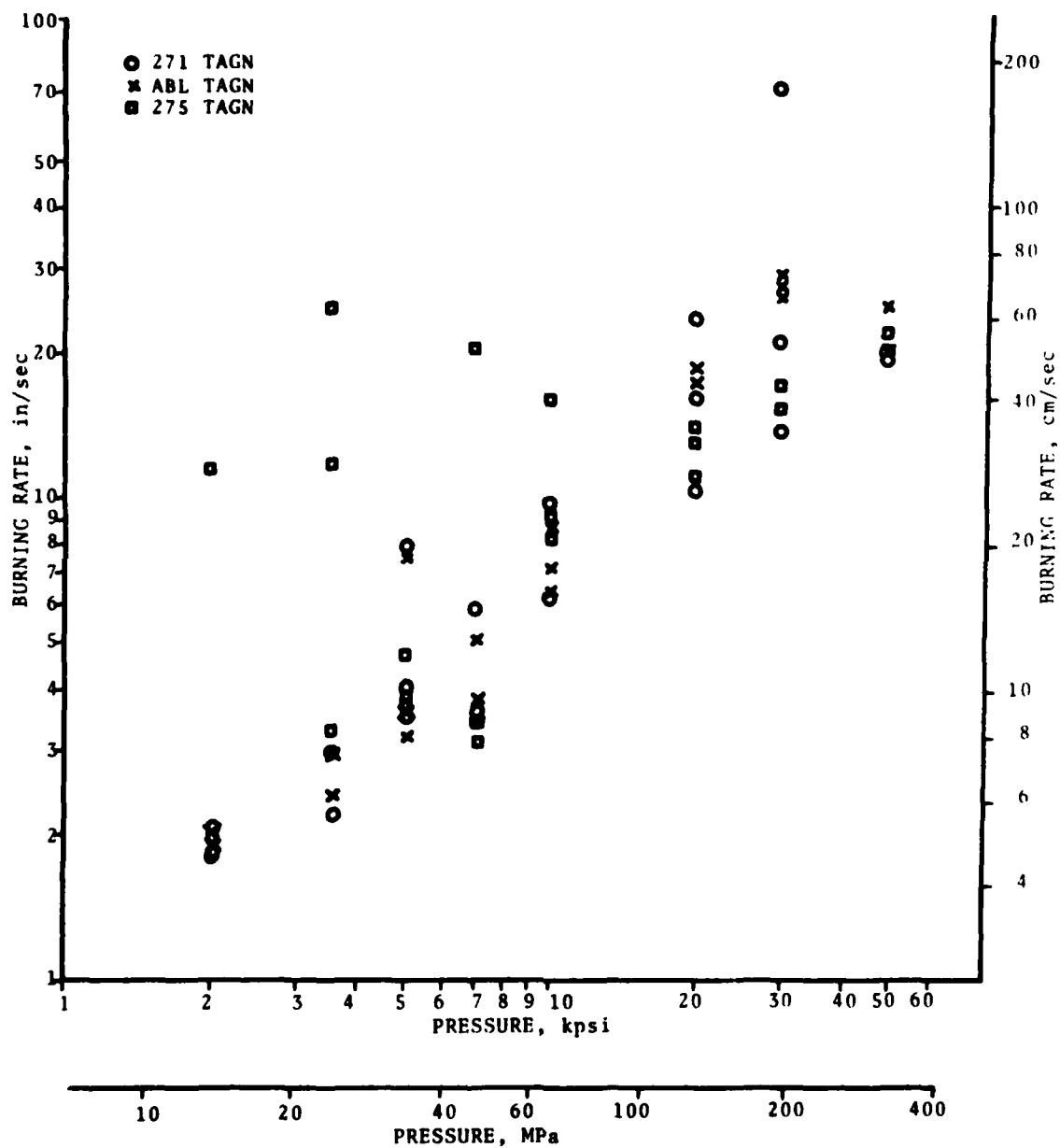


Figure 5. Burning Rates of Three Standard Formulated Propellants Containing TAGN (70 Percent) from Three Different Batches

noteworthy that propellants formulated from recrystallized TAGN under the same conditions and with identical compositions exhibited acceptable burning rate data (GP 200, GP 218 and GP 219 in Figure 4) and non-acceptable erratic burning rate data (2.7.1 in Figure 5).

Similarly, propellant (containing NC, 20 percent; IDP, 4.8 percent; TAGN, 45.0 percent; HMX, 29.8 percent;  $K_2SO_4$ , 0.2 percent and Resorcinol, 0.2 percent) manufactured at ABL and subjected to long term storage at 40° and 50°C also showed some erratic burning rate data which may be attributed to microporosity (Figure 6).

Further evidence of a TAGN induced incompatibility in propellant comes from the studies of Hartman et al (Reference 6) who noted that propellant made from colored TAGN became more acidic than propellant made from uncolored TAGN when undergoing accelerated aging at 70°C. As noted in Section II, solvent moist metal contaminated TAGN when heated at 60°C in a forced air oven was shown to turn pink then blue and give off acid fumes. It can be anticipated that propellant containing contaminated TAGN would become progressively more acidic when stored in hot, humid climates.

Reynolds and Gray (Reference 4) noted that propellants made from TAGN produced by the batch process (in glass lined equipment) consistently gave higher absolute and bulk densities than propellant made from TAGN produced by a continuous process (in stainless steel equipment). The latter propellants also consistently displayed faster burning rates than the former propellants. The density and burning rate data are consistent with microporosity in the propellants made from TAGN produced by the continuous process. Presumably the metal contaminated TAGN microporosity in the propellant is a result of some process related to heat assisted aerial oxidation of the TAGN.



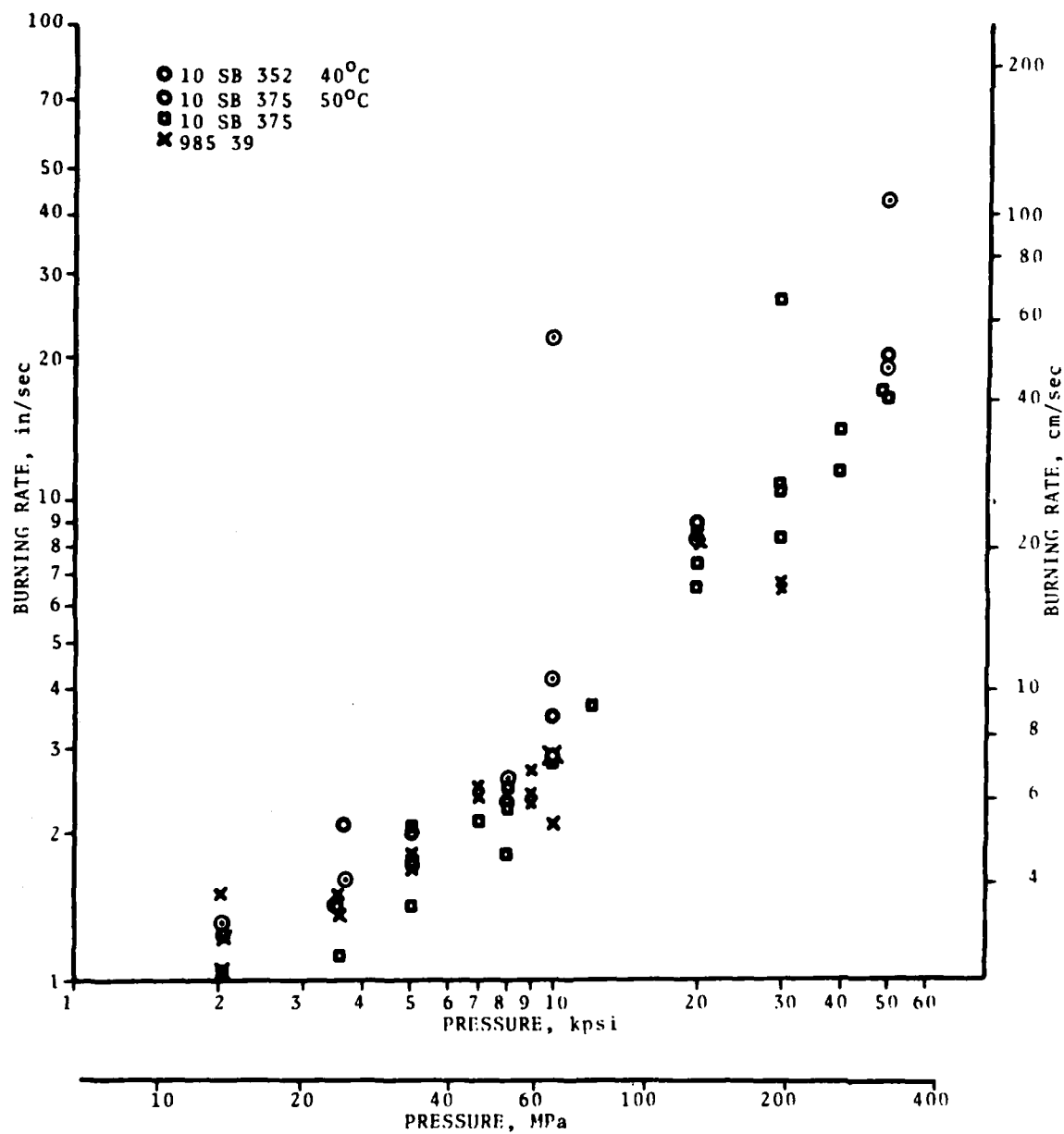


Figure 6. Burning Rates of Four Propellants Containing 45.0 Percent TAGN Manufactured at ABL Which Show Burning Rate Scatter

## SECTION IV

### CONCLUSIONS

The formation of highly colored impurities in TAGN results from the aerial oxidation of the free base, TAG. The rate of color formation in TAGN solutions is strongly catalyzed by some transition metal ions and basic media. A mechanistic scheme for color formation in TAGN has been proposed. The rate of formation of colored impurities in TAGN can be minimized by the rigorous exclusion of metal ions and by keeping solutions acidic to minimize the concentration of TAG. The use of an inert atmosphere (e.g. nitrogen) is also recommended, especially during synthesis of TAGN.

Propellant made from contaminated TAGN can undergo color changes during manufacture. Highly contaminated TAGN can produce unacceptable colored propellant containing highly colored macroscopic voids. Slightly contaminated TAGN may produce light brown or tan colored propellant which exhibits enhanced and erratic burning rate data resulting from microporosity in the propellant. However, sometimes tan colored propellant can produce reproducible and consistent burning rate data. The long term stability of propellant containing impure TAGN could be suspect in hot humid climates.

Strategies to minimize TAGN related incompatibilities in propellant include dry grinding of the TAGN, storage and recrystallization of TAGN in deionized acidified water, and drying of TAGN in a vacuum oven or inert atmosphere if feasible. Probably the most important factor in the production of acceptable propellant is the initial purity of the TAGN itself which can only be maintained by rigorous exclusion of metal ions and preferably an inert atmosphere during the synthesis of TAGN. The most accessible solvent for synthesis recrystallization and storage of TAGN is deionized water (acidified water for the latter two processes).

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